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(54) Rechargeable electrochemical cell

Wiederaufladbare elektrochemische Zelle

Pile électrochimique rechargeable

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- **EXTENDED ABSTRACTS, vol.86-2, no.18, SAN DIEGO page 28-29 J. J. AUBURN ET AL. 'LITHIUM INTERCALATION CELLS WITHOUT METALLIC LITHIUM: MO2/LICOO2 AND WO/LICOO2'**

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Description

FIELD OF THE INVENTION

[0001] The invention relates to rechargeable electrochemical alkali-metal cells such as rechargeable lithium batteries.

BACKGROUND OF THE INVENTION

[0002] Various non-aqueous alkali-metal electrochemical cells such as lithium cells are known in the art. Lithium cells, such as the one described in US Patent 4,828,834 to Nagaura et al. typically comprise a highly electroactive anode in the from of metallic lithium, a lithium salt dissolved in one or more organic solvents as the electrolyte, an electrochemically active cathode, which may be a chalogenide of a transition metal or a metal oxide and a semipermeable separator placed between the anode and the cathode. The separator acts as a mechanical barrier against short-circuiting.

[0003] One drawback of lithium cells is that since metallic lithium is a highly reactive metal, it readily reacts with water vapor in air, and thus, lithium anodes must be manufactured in an entirely dry atmosphere.

[0004] Another drawback of lithium cells is the formation of lithium dendrites during the charge/discharge cycle. Lithium dendrites react with the electrolyte to form electrochemically non-active species which do not participate in subsequent charge/discharge cycles. This leads to lower discharge efficiency. Further, lithium dendrites can bridge the gap between the cathode and the anode and therefore cause cell failure via internal short-circuiting.

[0005] One way which partially overcomes low cell efficiency resulting from lithium dendrites formation is to resort a large excess of lithium in the cell, typically a four fold excess. Lithium excess in the cell increases the thickness of the anode which is typically 150 - 200 microns in an AA size cell. As there exists a correlation between overall anode area and attainable power of the cell, the comparatively thick metallic lithium leads to a relatively low surface area and therefore to relatively low power density for the charge and for the discharge cycle. In addition, lithium excess in the cell reduces overall cell capacity, the larger lithium quantity is inherently more dangerous, and as lithium is comparatively expensive, cell cost is increased.

[0006] One approach to decrease dendrite formation is mechanical packaging under high pressure described in US Patent 4,902,589 to Dahn et al. A different approach is to charge the cell at relatively low current density, typically 0.3 mA/cm^2, which results in long charging times.

[0007] A different type of rechargeable lithium cells such as the one described in PCT Application PCT/CA90/00127 to Fong et al. include an anode comprising a suitable carbon form, such as coke or graphite, intercalated with lithium ions to form $Li_x C_6$, where x is lower than 1.

[0008] A drawback of lithium cells based on anodes made of lithium intercalated with carbon is that the maximum capacity derivable from such a cell is about 377 mAh/g which is considerably lower than the theoretical value of 3860 mAh/g for pure lithium metal. AA cells with a graphite intercalated anode such as the one described in US Patent 4,423,125 to Samar have a maximum capacity of the order of 500 mAh compared with 700 mAh for a cell with a lithium anode.

[0009] GB-A-2243566 describes a porous lithium electrode for a battery which includes a negative electrode of lithium metal or lithium alloy, a positive electrode and an electrolyte. The lithium metal or lithium alloy of the negative electrode has a bulk density no greater than 75% that of standard lithium and no less than 25% that of standard lithium, whereby the effective surface area of lithium metal or lithium alloy exposed to the electrolyte is increased.

[0010] DE-A-2834485 discloses a rechargeable cell which in the charged state has a lithium-containing anode, a solid cathode and an anhydrous organic electrolyte containing a lithium-containing salt. The lithium is incorporated in a light metal which forms the anode by electrochemical alloying.

[0011] WO-A-91/14025 discloses a process for the electrodeposition of lithium which comprises plating on to a primary cathode in a bath of lithium ions in solution with an organic solvent and using a supplementary cathode to neutralise by-products detrimental to the process. Lithium chloride and lithium hexafluoroarsenate may be used to provide the lithium ions.

[0012] It is an object of the present invention to provide an improved rechargeable electrochemical cell. There is thus provided according to one aspect of the invention a rechargeable electrochemical cell comprising a first electrode capable of reversibly incorporating a layer of an alkali metal on a surface thereof; a second electrode capable of reversibly incorporating therein alkali metal ions; and an electrolyte in contact with and separating the first and second electrodes, characterised in that the cell is in an uncharged state and the first electrode is made of copper, nickel, stainless steel or an electron conducting polymer, or is made of a metal coated with copper, nickel, stainless steel, chromium or gold and in that in use a layer of the alkali metal is plated on the surface of the first electrode during charging, whereby the internal pressure in the cell is increased such that alkali metal dendrite formation is reduced.

[0013] Further, there is provided according to another aspect of the invention a method of making a rechargeable electrochemical cell comprising the steps of assembling within a cell housing a first electrode having a surface substantially free from an alkali metal, a second electrode incorporating ions of said alkali metal therein and an electrolyte in contact with and separating the first and second electrodes; and applying an external electrical current to the cell, thereby plating the surface of the first electrode with said alkali metal which is transferred as ions from the second electrode to the surface of the first electrode through the electrolyte, the method being characterised in that the increase in the thickness of the first electrode due to the plating of the alkali metal increases the internal pressure in the cell, thereby reducing the alkali metal dendrite formation.

[0014] In one embodiment, the assembly in the housing contains a first electrode comprising a sandwich like structure of a film which is essentially free of lithium, a second electrode incorporating lithium ions therein, a non-conductive porous separator therebetween and a non-aqueous electrolyte in contact with the first and second electrodes and the separator.

[0015] Further, in accordance with another aspect of the invention the electrolyte is a non-aqueous solvent having therein a salt of said alkali metal such as $LiAsF_6$, $LiBF_4$ and $LiClO_4$ or it is in an ion conducting polymer, and the cell assembled with the non-aqueous solvent may also include porous non-conducting material for separating the first and second electrodes.

[0016] Finally, in accordance with another aspect of the invention the thickness of the first electrode is about 5 to 50 µm (microns) and the cell is characterised in that the thickness of the first electrode is considerably lower than the thickness of the second electrode.

[0017] The present invention will be understood and appreciated more fully from the following detailed description taken in conjunction with the appended sole figure of the drawing which is a schematic cross section of a spiral wound type cell, constructed and operative in accordance with a preferred embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0018] As illustrated in the drawing, a rechargeable electrochemical cell 10 according to one preferred embodiment of the present invention preferably comprises an anode 12 described in detail below, a non-aqueous lithiated electrolyte 14, a non-conductive microporous separator 16 and a cathode 18, such as an aluminum net supporting a lithiated metal oxide. The lithiated metal oxide can be a lithiated cobalt oxide, applied under pressure to both surfaces of such netting. Alternatively, the electrolyte and the non-conductive porous separator are replaced with a solid polymer electrolyte based on PVC/PC doped with lithium salt such as the one described in US Patent 5,252,413 to Alamgir.

[0019] The anode in a cell according to a preferred embodiment of the present invention preferably comprises a support which is a thin conductive film on the surface of which a layer of an alkali metal, preferably lithium, is plated in-situ during charging of the cell in which the anode is fabricated.

[0020] The thin conductive film can be a metallic film such as copper, nickel or a stainless steel film. Alternatively, the thin conductive film can be a metal coated by another metal such as copper, nickel or stainless steel or it can be coated by chromium or gold. The thin conductive film can also be an electronic conductive polymer.

[0021] The thickness of the thin conductive film is preferably 5 - 50 µm (microns) and more preferably 8 - 20 µm (microns) in comparison with typical thicknesses of 150 - 200 µm (microns) of the cathode of prior art anodes. The advantageous mechanical properties of metals such as nickel, copper, stainless steel and electronic conductive polymer make it possible to use foils of only about 10 to 15 µm (microns) thickness and thus to attain a high overall surface area. For example, there were tried AA size cells with an anode area of about 400cm^2, and such cells can be charged at comparatively high current, during a short charge time. Furthermore, the copper foil is less expensive than a lithium foil which is considerably thicker. The thin anode leaves space for a comparatively thicker cathode. This results in cell yielding high capacity and energy.

[0022] A preferred method for making a cell of the present invention is described with reference to a spiral wound type cell. It is to be appreciated that the method is not limited to a spiral wound type cell and is applicable to any type of cell. In order to fabricate such a cell, for example an AA size battery, a can made by any appropriate material such as nickel plated steel is used as the cell housing 20. Then, a sandwich like laminar structure is assembled made of a layer of any of the foils described above to be used as the anode support, a layer of the permeable non-conductive porous separator and a layer of a lithium based cathode. Then, the layered structure is wound onto an inner core (not shown) affixed in the cell housing. Next, the electrolyte is introduced and finally the a cap 22 is sealed to the can.

[0023] It is a particular feature of the present invention that the anode can be prepared in any environment. This is since the foil which is used for the anode support is essentially free from lithium before charging, and therefore there is no need to seclude the anode from the atmosphere.

[0024] Cells of the present invention are assembled in the uncharged state, and the charging of the cell is the first step when the cell is to be used. During the charging of the cell ions from the cathode pass via the electrolyte to the anode, and by this process lithium is plated on the support surfaces and a thin layer of lithium is formed thereon.

Typically, the lithium layer would be 5 to 10 µm (microns). Consequently, the overall thickness of the anode increases and this leads to an increase of the entire stack, and as this stack is confined in a case, the cell housing, internal pressure increases between the components. This pressure increase reduces dendrite formation. This minimizes the excess of lithium required and thus cell safety and overall energy obtainable from such cells are improved.

[0025] The following examples illustrate, but do not limit, certain aspects of the present invention.

EXAMPLE 1

[0026] An AA size test cell was fabricated using the following components:

[0027] A copper foil 15 microns thick was used as the anode support.

[0028] The cathode is made of $LiCoO_2$ pressed on both sides of aluminum foil support. Five weight percent graphite was used as a conductive material, and PVDF as binder.

[0029] Microporous polypropylene, "Celgard" type 3402 separating and disposed between the anode and the cathode. 1 Molar $LiAsF_6$ in a mixture of 1,3-dioxolane and tetrahydrofuran (THP) was used as an electrolyte.

[0030] The cell stack (the anode support, separator and the cathode) was assembled in a spiral wound configuration and inserted into a can made of nickel plated steel. The cover was hermetically sealed to the can by plasma welding. The electrolyte was introduced to the cell through a 1mm opening in the can bottom. This was followed by resistance welding.

[0031] The thickness of the anode support was 15 microns, its width 40mm and its length 550mm. The cathode had the same width and length as the anode, but its thickness was much higher, 180 microns. This results in a potential electrode area of 440cm^2.

[0032] About 1 hour after filling the electrolyte cell open circuit voltage (hereafter OCV) stabilized at a value of 0.32volt.

[0033] The cell was charged by an average current of 250mA. During charging cell voltage increased rapidly reaching a value of 3.9V in 5 minutes. The cell reached a 4.1 volt cut-off value after 5.5 hours. The cell was discharged under a current of 250mA giving a capacity of 1.2Ah to 3.4 volt cut-off (at least 95% depth of discharge, hereafter DOD). The average working voltage was 3.8V. This lead to an energy density of more than 500Wh/L. After 10 deep charge/discharge cycles (at least 95% DOD) cell capacity decreased to 930mAh. Cell capacity was above 830mAh after 30 cycles.

COMPARATIVE EXAMPLE

[0034] A controlled AA size cell having 4 fold excess of lithium metal was constructed. The width of the anode and the cathode was 40mm as in the cell of Example 1. The anode, however, was significantly thicker, 170 µm (microns), in comparison to only 15 µm (microns) in the cell of Example 1. The length of the cathode and the anode was 270mm. Therefore the electrode surface area was 216 cm^2.

[0035] The cell was charged and discharged at a current of 250mA as in the case of the test cell. In the first discharge cycle the cell delivered only 640mAh. Cell capacity decreased to 450mA after 10 cycle. The cell was internally shorted during the charge process of cycle 24. This shorting occurred most likely due to the high charging current density which was 1.16mA/cm^2 in the control cell, in comparison to 0.57mA/cm^2 in the cell of Example 1.

EXAMPLE 2

[0036] A cell was made as the cell of Example 1, except that the anode support was made of a nickel foil 25 µm (microns) thick, and the cathode thickness was 170 µm (microns).

[0037] The cell was charged and discharged under the same profile as in Example 1. In the first discharge cycle cell capacity was 1.1Ah. This value gradually decreased to 0.95Ah after 10 cycles.

EXAMPLE 3

[0038] A cell was made as the cell of Example 1 except that the anode support was made of 15 microns copper coated with 3 µm (microns) of nickel on each side. The cell OCV was 0.35V. The cell was charged and discharged under the same profile as in Example 1 giving a capacity of 1.1Ah in the first discharge cycle. Capacity decreased to a value of 0.8Ah after 10 cycles.

EXAMPLE 4

[0039] A cell was made as the cell of Example 1 except that the cathode contained $LiNiO_2$ as active material. Open cell circuit potential was 0.75 Volt. Under the same charge/discharge regime as in Example 1 the cell delivered 0.95Ah in the first cycle. a value that decreased to 0.70Ah after 10 cycles.

EXAMPLE 5

[0040] A cell was made as the cell of Example 2 except that the cathode was made of $LiNiO_2$ as active material. The cell OVCV was 0.6V. Under the same charge/discharge profile of Example 2 the cell delivered 1.0Ah at the first discharge. Cell capacity decreased to 0.9Ah after 10 cycles.

EXAMPLE 6

[0041] A cell was made as the cell of Example 1 except that the cathode was made of $LiMn_2O_4$ as active material. The cell OCV was 0.7V. Under the same charge/discharge profile as in Example 1 the cell delivered 850mAh in the first discharge, a value which decreased to 800mAh after 10 cycles.

EXAMPLE 7

[0042] A cell was made as the cell of Example 1 except that the electrolyte was 1 Molar of $LiBF_4$ in a mixture of 1,3-dioxolane and THF. The cell OCV was 0.35V. Under the same charge/discharge profile as in Example 1 the cell delivered 1.2Ah in the first discharge. The capacity in cycle No. 10 decreased to 0.85Ah.

EXAMPLE 8

[0043] A cell was made as the cell of Example 1 except that the electrolyte was 1.0 Molar of $LiClO_4$ in a mixture of propylene carbonate (PC) and diethyl carbonate (DEC). The cell OCV was 0.40V. The cell was charged and discharged at the same regime of Example 1, except that the cut-off charge voltage was 4.2V.

[0044] The cell delivered 1.25Ah in the first discharge. Cell capacity decreased to 0.60Ah at the 10th cycle.

EXAMPLE 9

[0045] A cell was made as the cell of Example 1. After charging the cell was disassembled. A uniform lithium plating on the copper foil was observed.

EXAMPLE 10

[0046] A laboratory type cell (Y. Geronov et al. J. of Electrochemical Society 137 (1990) 3338) was fabricated using a copper foil as the anode support, a solid polymer electrolyte based on PVC/PC doped with lithium salt and a lithium cobalt oxide based cathode as source for lithium ions.

[0047] The thickness of the copper foil was 15 microns, the solid polymer electrolyte 70 μm (microns) and the lithium cobalt oxide based cathode 100 μm (microns). The active surface area was about 1 cm^2. Cell conductivity at 1000Hz was 1.0 mMho at room temperature. The cell was charged with current density of 0.1mA/cm2 at 60 degrees Celsius. During charging the cell voltage raised to 3.95V after 30 minutes and stabilized at 4.05V after 7 hours. The cell was discharged under the same current density for 3 hours to 3V cut off value reaching an efficiency of 37%.

EXAMPLE 11

[0048] A cell was made as the cell of Example 10. After chargimg the cell was disassembled. A uniform lithium plating on the copper foil was observed.

[0049] Table 1 below summarizes experimental conditions and results of the above Examples 1 - 11.

[0050] It will be appreciated by persons skilled in the art that the present invention is not limited by what has been particularly shown and described hereinabove. Rather the scope of the invention is defined by the claims which follow:

TABLE I

Example	Anode	Cathode	Electrolyte	Solvent	OCV (V)	Charge cut-off Voltage	Capacity (Ah) 1st cycle	Capacity (Ah) 10th cycle
1	Copper	$LiCoO_2$	$LiAsF_6$	1,3 dioxolane THF	0.32	4.1	1.2	0.93
2	Nickel	$LiCoO_2$	$LiAsF_6$	1,3 dioxolane THF	0.40	4.1	1.1	0.95
3	Nickel plated on copper	$LiCoO_2$	$LiAsF_6$	1,3 dioxolane THF	0.35	4.1	1.2	0.80
4	Copper	$LiNiO_2$	$LiAsF_6$	1,3 dioxolane THF	0.75	4.1	0.95	0.70
5	Nickel	$LiNiO_2$	$LiAsF_6$	1,3 dioxolane THF	0.60	4.1	1.0	0.90
6	Copper	$LiMn_2O_4$	$LiAsF_6$	1,3 dioxolane THF	0.70	4.1	0.85	0.80
7	Copper	$LiCoO_2$	$LiBF_4$	1,3 dioxolane THF	0.35	4.1	1.20	0.85
8	Nickel	$LiCoO_2$	$LiClO_4$	PC DEC	0.40	4.2	1.25	0.60
9	Copper	$LiCoO_2$	$LiAsF_6$	1,3 dioxolane THF	0.38	4.1	0.9	---
10	Copper	$LiCoO_2$	PVC/PC	$LiClO_4$	0.30	4.05	0.0003	---
11	Copper	$LiCoO_2$	PVC/PC	$LiClO_4$	0.30	4.05	---	---

Claims

1. A rechargeable electrochemical cell (10) comprising:

   a first electrode (12) capable of reversibly incorporating a layer of an alkali metal on a surface thereof;
   a second electrode (18) capable of reversibly incorporating therein alkali metal ions; and
   an electrolyte (14) in contact with and separating the first (12) and second (18) electrodes, characterised in that the cell is in an uncharged state and the first electrode (12) is made of copper, nickel, stainless steel or an electron conducting polymer, or is made of a metal coated with copper, nickel, stainless steel, chromium or gold and in that in use a layer of the alkali metal is plated on the surface of the first electrode (12) during charging, whereby the internal pressure in the cell (10) is increased such that alkali metal dendrite formation is reduced.

2. A rechargeable cell according to claim 1, wherein the alkali metal consists essentially of lithium.

3. A rechargeable cell according to claim 1 or claim 2, wherein the electrolyte (14) is either a non-aqueous solvent having therein a salt of said alkali metal or a solid ion conducting polymer.

4. A rechargeable cell according to any one of the preceding claims and further comprising a porous non-conductive

separator (16) separating the first (12) and second (18) electrodes.

5. A rechargeable cell according to any one of the preceding claims, wherein the thickness of the first electrode (12) is from 5 to 50 µm (microns).

6. A rechargeable cell according to claim 3, wherein the non-aqueous solution is $LiAsF_6$, $LiBF_4$ or $LiClO_4$.

7. A rechargeable cell according to any one of the preceding claims, wherein the thickness of the first electrode (12) is considerably lower than the thickness of the second electrode (18).

8. A method of making a rechargeable electrochemical cell (10) comprising the steps of:

   assembling within a cell housing (20) a first electrode (12) having a surface substantially free from an alkali metal, a second electrode (18) incorporating ions of said alkali metal therein and an electrolyte (14) in contact with and separating the first (12) and second (18) electrodes; and
   applying an external electrical current to the cell, thereby plating the surface of the first electrode with said alkali metal which is transferred as ions from the second electrode (18) to the surface of the first electrode through the electrolyte (14), the method being characterised in that the increase in the thickness of the first electrode (12) due to the plating of the alkali metal increases the internal pressure in the cell (10), thereby reducing alkali metal dendrite formation.

9. A method according to claim 8, wherein said alkali metal consists essentially of lithium.

10. A method according to claim 8 or claim 9, comprising forming the electrolyte (14) either as a non-aqueous solvent having therein a salt of said alkali metal or as a solid ion conducting polymer.

11. A method according to any one of claims 8 to 10, comprising forming the cell wherein a porous non-conductive porous separator (16) separates the first (12) and second (18) electrodes.

12. A method according to claim 8, wherein the assembly in the cell housing contains a first electrode (12) comprising a sandwich-like structure of a film which is essentially free of lithium, a second electrode (18) incorporating lithium ions therein, a non-conductive porous separator (16) therebetween and a non-aqueous electrolyte (14) in contact with the first (12) and second (18) electrodes and the separator (16).

13. A method according to any one of claims 8 to 12, wherein the surface of the first electrode (12) is a conducting metal.

14. A method according to any one of claims 8 to 13, wherein the first electrode (12) is made of a material selected from copper, nickel and stainless steel.

15. A method according to any one of claims 8 to 13 wherein the first electrode (12) is made of a metal coated with copper, nickel, stainless steel, chromium or gold.

16. A method according to any one of claims 8 to 12, wherein the first electrode (12) is made of an electron conducting polymer.

17. A method according to any one of claims 12 to 16, comprising forming the electrolyte (14) either as a non-aqueous solvent having therein a salt of lithium or as a solid ion conducting polymer.

18. A method according to any one of claims 8 to 17, wherein the first electrode (12) has a thickness of from 5 to 50 µm (microns).

19. A method according to claim 10 or claim 12, wherein the non-aqueous solution is $LiAsF_6$, $LiBF_4$ or $LiClO_4$.

Patentansprüche

1. Wiederaufladbare elektrochemische Zelle (10), umfassend: eine erste Elektrode (12), die an ihrer Oberfläche eine Schicht eines Alkalimetalls reversibel inkorporieren kann; eine zweite Elektrode (18), die in ihrem Inneren Alkali-

metallionen reversibel inkorporieren kann;
und
einen Elektrolyten (14), der mit der ersten (12) und zweiten (18) Elektrode in Kontakt ist und diese trennt, dadurch **gekennzeichnet,** daß die Zelle im ungeladenen Zustand ist und die erste Elektrode (12) aus Kupfer, Nickel, Edelstahl oder einem elektronenleitenden Polymer besteht oder aus einem mit Kupfer, Nickel, Edelstahl, Chrom oder Gold beschichteten Metall besteht, und daß im Betrieb während des Ladens eine Schicht des Alkalimetalls auf der Oberfläche der ersten Elektrode (12) galvanisch abgeschieden wird, wobei der Innendruck in der Zelle (10) erhöht wird derart, daß eine Dendritbildung des Alkalimetalls reduziert wird.

2. Wiederaufladbare Zelle nach Anspruch 1,
bei der das Alkalimetall im wesentlichen aus Lithium besteht.

3. Wiederaufladbare Zelle nach Anspruch 1 oder 2,
bei der der Elektrolyt (14) entweder ein nichtwässriges Lösungsmittel, das ein Salz des Alkalimetalls enthält, oder ein ionenleitender Festkörperpolymer ist.

4. Wiederaufladbare Zelle nach einem der vorangehenden Ansprüche, die ferner einen porösen nichtleitfähigen Separator (16) enthält, der die erste (12) und zweite (18) Elektrode trennt.

5. Wiederaufladbare Zelle nach einem der vorangehenden Ansprüche, bei der die Dicke der ersten Elektrode (12) 5 bis 50 μm (Mikron) beträgt.

6. Wiederaufladbare Zelle nach Anspruch 3,
bei der die nichtwässrige Lösung $LiAsF_6$, $LiBF_4$ oder $LiClO_4$ ist.

7. Wiederaufladbare Zelle nach einem der vorangehenden Ansprüche, bei der die Dicke der ersten Elektrode deutlich niedriger als die Dicke der zweiten Elektrode (18) ist.

8. Verfahren zum Herstellen einer wiederaufladbaren elektrochemischen Zelle (10), mit den Schritten:

Zusammenstellen, in einem Zellengehäuse (20), einer ersten Elektrode (12) mit einer von Alkalimetall im wesentlichen freien Oberfläche, einer zweiten Elektrode (18), die Ionen des Alkalimetalls inkorporiert hat, und eines Elektrolyten (14), der mit der ersten (12) und zweiten (18) Elektrode in Kontakt ist und diese trennt; und Anlegen eines äußeren elektrischen Stromes an die Zelle und dadurch galvanisches Beschichten der Oberfläche der ersten Elektrode mit dem Alkalimetall, welches in Form von Ionen von der zweiten Elektrode (18) zur Oberfläche der ersten Elektrode durch den Elektrolyten (14) überführt wird, wobei das Verfahren dadurch **gekennzeichnet** ist,
daß die Dickenzunahme der ersten Elektrode (12) aufgrund des galvanischen Abscheidens des Alkalimetalls den Innendruck in der Zelle (10) erhöht und dadurch die Dendritbildung des Alkalimetalls reduziert.

9. Verfahren nach Anspruch 8,
bei dem das Alkalimetall im wesentlichen aus Lithium besteht.

10. Verfahren nach Anspruch 8 oder 9,
bei dem der Elektrolyt (14) entweder als nichtwässriges Lösungsmittel, das ein Salz des Alkalimetalls enthält, oder als ionenleitender Festkörperpolymer gebildet wird.

11. Verfahren nach einem der Ansprüche 8 bis 10,
bei der die Zelle so geformt wird, daß ein poröser nichtleitfähiger Separator (16) die erste (12) und zweite (18) Elektrode trennt.

12. Verfahren nach Anspruch 8,
bei dem die Anordnung in dem Zellengehäuse eine erste Elektrode (12) mit einer sandwichartigen Struktur eines im wesentlichen lithiumfreien Films, eine zweite Elektrode (18), in der Lithiumionen inkorporiert sind, einen dazwischen angeordneten nichtleitfähigen porösen Separator (16) und einen nichtwässrigen Elektrolyten (14) in Kontakt mit der ersten (12) und zweiten (18) Elektrode und dem Separator (16) enthält.

13. Verfahren nach einem der Ansprüche 8 bis 12,

bei dem die Oberfläche der ersten Elektrode (12) ein leitfähiges Metall ist.

14. Verfahren nach einem der Ansprüche 8 bis 13,
bei dem die erste Elektrode (12) aus einem aus Kupfer, Nikkel und Edelstahl ausgewählten Material besteht.

15. Verfahren nach einem der Ansprüche 8 bis 13,
bei dem die erste Elektrode (12) aus einem mit Kupfer, Nikkel, Edelstahl, Chrom oder Gold beschichteten Metall besteht.

16. Verfahren nach einem der Ansprüche 8 bis 12,
bei dem die erste Elektrode (12) aus einem elektronenleitenden Polymer besteht.

17. Verfahren nach einem der Ansprüche 12 bis 16,
bei dem der Elektrolyt (14) entweder als ein nichtwässriges Lösungsmittel, das ein Lithiumsalz enthält, oder als ionenleitender Festkörperpolymer gebildet wird.

18. Verfahren nach einem der Ansprüche 8 bis 17,
bei dem die erste Elektrode (12) eine Dicke von 5 bis 50 µm (Mikron) hat.

19. Verfahren nach Anspruch 10 oder 12,
bei dem die nichtwässrige Lösung $LiAsF_6$, $LiBF_4$ oder $LiClO_4$ ist.

Revendications

1. Cellule électrochimique rechargeable (10) comprenant :

   une première électrode (12) qui peut incorporer de manière réversible une couche d'un métal alcalin sur une surface de l'électrode,
   une seconde électrode (18) qui peut incorporer de manière réversible des ions de métaux alcalins, et
   un électrolyte (14) placé au contact de la première (12) et de la seconde (18) électrode et les séparant,

   caractérisée en ce que la cellule est à un état non chargé et la première électrode (12) est formée de cuivre, de nickel, d'acier inoxydable ou d'un polymère conducteur d'électrons, et est formée d'un métal revêtu de cuivre, de nickel, d'acier inoxydable, de chrome ou d'or, et en ce que, pendant l'utilisation, une couche de métal alcalin est déposée à la surface de la première électrode (12) pendant la charge, si bien que la pression interne de la cellule (10) augmente afin que la formation de dendrites de métaux alcalins soit réduite.

2. Cellule rechargeable selon la revendication 1, dans laquelle le métal alcalin est essentiellement le lithium.

3. Cellule rechargeable selon la revendication 1 ou 2, dans laquelle l'électrolyte (14) est un solvant non aqueux contenant un sel d'un métal alcalin ou un polymère solide conducteur d'ions.

4. Cellule rechargeable selon l'une quelconque des revendications précédentes, comprenant en outre un séparateur non conducteur poreux (16) séparant la première électrode (12) de la seconde (18).

5. Cellule rechargeable selon l'une quelconque des revendications précédentes, dans laquelle l'épaisseur de la première électrode (12) est comprise entre 5 et 50 µm.

6. Cellule rechargeable selon la revendication 3, dans laquelle la solution non aqueuse est $LiAsF_6$, $LiBF_4$ ou $LiClO_4$.

7. Cellule rechargeable selon l'une quelconque des revendications précédentes dans laquelle l'épaisseur de la première électrode (12) est considérablement inférieure à l'épaisseur de la seconde électrode (18).

8. Procédé de fabrication d'une cellule électrochimique rechargeable (10) comprenant les étapes suivantes :

   l'assemblage, à l'intérieur d'un boîtier de cellule (20), d'une première électrode (12) ayant une surface pratiquement dépourvue d'un métal alcalin, d'une seconde électrode (18) incorporant des ions du métal alcalin et d'un électrolyte (14) placé au contact de la première électrode (12) et de la seconde électrode (18) et séparant celles-ci, et

l'application d'un courant électrique extérieur à la cellule, si bien que la surface de la première électrode est revêtue du métal alcalin qui est transféré sous forme d'ions de la seconde électrode (18) à la surface de la première électrode par l'intermédiaire de l'électrolyte (14), le procédé étant caractérisé en ce que l'augmentation de l'épaisseur de la première électrode (12) due au dépôt du métal alcalin augmente la pression interne de la cellule (10) et réduit ainsi la formation de dendrites de métal alcalin.

9. Procédé selon la revendication 8, dans lequel le métal alcalin est essentiellement constitué de lithium.

10. Procédé selon la revendication 8 ou 9, comprenant la formation de l'électrolyte (14) soit sous forme d'un solvant non aqueux contenant un sel d'un métal alcalin soit sous formé d'un polymère solide conducteur ionique.

11. Procédé selon l'une quelconque des revendications 8 à 10, comprenant la formation de la cellule dans laquelle un séparateur non conducteur poreux (16) sépare la première électrode (12) de la seconde (18).

12. Procédé selon la revendication 8, dans lequel l'ensemble placé dans le boîtier de la cellule contient une première électrode (12) qui comprend une structure analogue à un sandwich d'un film qui est essentiellement dépourvu de lithium, une seconde électrode (18) qui contient des ions lithium, un séparateur poreux non conducteur (16) placé entre elles et un électrolvte non aqueux (14) placé au contact de la première électrode (12) et de la seconde électrode (18) et du séparateur (16).

13. Procédé selon l'une quelconque des revendications 8 à 12, dans lequel la surface de la première électrode (12) est un métal conducteur.

14. Procédé selon l'une quelconque des revendications 8 à 13, dans lequel la première électrode (12) est formée d'un matériau choisi parmi le cuivre, le nickel et l'acier inoxydable.

15. Procédé selon l'une quelconque des revendications 8 à 13, dans lequel la première électrode (12) est formée d'un métal revêtu de cuivre, de nickel, d'acier inoxydable, de chrome ou d'or.

16. Procédé selon l'une quelconque des revendications 8 à 12, dans lequel la première électrode (12) est formée d'un polymère conducteur d'électrons.

17. Procédé selon l'une quelconque des revendications 12 à 16, comprenant la formation de l'électrolyte (14) soit sous forme d'un solvant non aqueux contenant un sel de lithium soit sous forme d'un polymère solide conducteur ionique.

18. Procédé selon l'une quelconque des revendications 8 à 17, dans lequel la première électrode (12) a une épaisseur comprise entre 5 et 50 µm.

19. Procédé selon la revendication 10 ou 12, dans lequel la solution non aqueuse est $LiAsF_6$, $LiBF_4$ ou $LiClO_4$.

FIG.1